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SCIENTIFIC CRITERIA DOCUMENT FOR THE DEVELOPMENT OF AN INTERIM PROVINCIAL WATER QUALITY OBJECTIVE FOR THALLIUM

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AN INTERIM PROVINCIAL WATER QUALITY OBJECTIVE

FOR THALLIUM

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PREFACE

The Ontario Ministry of Environment and Energy develops Provincial Water Quality Objectives or Interim Objectives for those substances deemed to be of environmental concern in Ontario as determined through a screening process which considered persistence, potential to bioaccumulate, acute and chronic toxicity and potential presence in the aquatic environment. Alternatively, Ministry staff who have a direct responsibility for managing possible effects of these chemicals may request an evaluation. Provincial Water Quality Objectives and Interim Objectives (PWQO/IPWQO) are numeric or narrative criteria intended to protect all life stages of aquatic organisms for indefinite exposures and/or to protect recreational uses of water. PWQO/IPWQO for recreational uses, including swimming, are currently based on microbiological and aesthetic considerations. The potential for harmful effects from exposure to chemical substances during recreational uses is unknown at present, but will be considered when scientific information becomes available. Ontario Drinking Water Objectives and sport fish consumption guidelines are also considered in protection of human health.

PWQO/IPWQO represent a desirable water quality for the protection of designated uses of surface waters in Ontario. Objectives/Interim Objectives do not take into account analytical detection or quantification limits, treatability or removal potential, socio-economic factors, natural background concentrations, or potential transport of contaminants among air, water and soil. These factors are considered in policies and procedures which govern the uses of PWQO/IPWQO, contained in the booklet, Water Management: Policies, Guidelines, Provincial Water Quality Objectives of the Ministry of Environment and Energy (OMOEE 1994), which deals with all aspects of Ontario's water management policy.

The process for deriving these criteria is detailed in Ontario's Water Quality Objective Development Process (1992). The toxicology literature is reviewed for all of the following areas: aquatic toxicity, bioaccumulation, mutagenicity and aesthetic considerations. The final Objective/Interim Objective is based on the lowest effect concentration reported for any of these factors on aquatic organisms as well as taste and odour considerations of the water. Where there are reliable and adequate data, an Objective is developed using a safety factor. Where there are fewer data, an Interim Objective is developed using an "uncertainty factor".

The size of the uncertainty factor reflects the availability of appropriate data and the potential of the material to bioaccumulate. The uncertainty factor used in Ontario's procedures based on this lack of data sometimes produces Interim Objectives considerably lower than those of other agencies that do not use this approach. Interim Objectives can be promoted to Objectives when sufficient reliable data become available.

PWQO/IPWQO are used to designate surface waters of the Province which should not be further degraded. They are also used in receiving water discharge assessments and may be included in Certificates of Approval which are issued to regulate effluent discharges. Where better water quality is required to protect other beneficial uses of the environment in a given location, appropriate criteria and factors, including public health considerations, are taken into account.

SUMMARY

Thallium, a group IIIb metal in the periodic table, is neither mined nor refined in Ontario, but has been detected in effluents and surface waters. Thallium is used in the manufacture of alloys, specialized glassware and photocells. It may enter surface waters through natural weathering of rocks. Man-made sources include mining activities, sulphuric acid manufacture by pyrites roasting, smelting activities and fly ash emissions from coal-fired generating plants. Surface water concentrations ranging from 0.001 to 0.1 mg/L have been reported across Canada, but there are few recent data. The current OMOEE analytical detection limit is 0.01 mg/L. The aquatic chemistry of thallium is not well known. Oxidation states are 1+ (more common) and 3+. Biomethylation has been demonstrated, but has apparently not been detected in surface waters. Fate of thallium in freshwater systems is not well studied, but it may be removed from surface waters through incorporation into sediments or biological organisms or through dilution and flushing.

The literature (current to May 1993) indicated that acute effects for a variety of aquatic life from thallium ranged between 0.86 and 132 mg/L. Chronic effects ranged from 0.008 to 40.8 mg/L.

Thallium does not appear to bioaccumulate to any significant degree in fish; bioconcentration factors (BCFs) are generally <150. Higher BCFs, however, have been reported in some aquatic insects.

An Interim Provincial Water Quality Objective (IPWQO) is derived herein for the protection of aquatic life. Physical-chemical properties, aquatic toxicity, bioaccumulation potential, taste and odour characteristics and genotoxicity potential of thallium were considered in the development of the IPWQO.

The IPWQO was calculated by dividing the lowest adverse effect concentration, 28 d phytotoxicity to duckweed (*Lemna minor*) at 0.008 mg/L, by the final uncertainty factor of 24.

The recommended Interim Provincial Water Quality Objective for thallium is 0.0003 mg/L.

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Notes and abbreviations used in the text

>	greater than
<	less than
%	percent
ACR	acute-to-chronic-ratio. This is a ratio of an acute effect to a chronic no effect concentration. It is used to extrapolate no effect concentrations in other species.
BCF	bioconcentration factor - the ratio formed by dividing the concentration of a chemical in an organism or its tissues by the concentration in the water
$CaCO_3$	calcium carbonate
Cl, Cl^-	chlorine, chloride ion
clastogen	a substance with the ability to cause breaks or rearrangements in chromosomal material
EC50	effect concentration - the concentration of a chemical in water which causes an effect in half the test population. Common effects are growth and reproduction.
EMPPL	Effluent Monitoring Priority Pollutant List
HCO_3^-	bicarbonate ion
ICP (ICP/MS)	inductively coupled plasma emission spectroscopy (mass spectrometry)
ILL	incipient lethal level - the waterborne concentration of a chemical which would just effect 50% of a test population exposed for a infinitely long time.
IRIS	integrated risk information system (an on-line database)
LC50	waterborne chemical concentration lethal to 50% of the test population within a given time period, i.e. 24h.
LOEC	lowest observed effect concentration - the lowest concentration in a test series which caused an observable effect compared with an untreated group of test organisms
MATC	maximum-acceptable-toxicant-concentration. The geometric mean of the LOEC and the NOEC.
MISA	Municipal-Industrial Strategy for Abatement - a treatment-technology based program for controlling point source waste discharges.
mutagen	a substance capable of causing heritable changes in genetic material in either reproductive or other cells.
NOEC	no observed effect concentration - the highest concentration in a test series in which the test organisms fared no differently than the untreated group
teratogen	a substance capable of causing birth defects or altering the normal development of cells, tissues or organs
SO_4^{2-}	sulphate ion
Tl, Tl^+	thallium, thallim ion

Units of measure

m	metre
cm	centimetre
mm	millimetre
d	day
h	hour

Concentrations in this document are expressed in a number of different units commonly used in scientific papers. The conversion factors are:

1 gram per litre (g/L)	=	1000 milligrams per litre (mg/L)
1 mg/L (or parts per million)	=	1000 micrograms per litre (µg/L)
1 µg/L (or parts per billion)	=	1000 nanograms per litre (ng/L)

Similarly, 1 milligram per kilogram (mg/kg, or parts per million) = 1000 µg/kg (or parts per billion)

nmol/mL = nanogram molecular weight per millilitre of solution

1.0 INTRODUCTION

The Ontario Ministry of Environment and Energy (OMOEE) has the mandate to develop and revise Policies, Guidelines, and Provincial Water Quality Objectives to protect the Province's water resources. The Policies and Guidelines are designed to assure that "...surface waters in the Province are of a quality which is satisfactory for aquatic life and recreation." (see OMOE 1992b, OMOEE 1994). Numerical Objectives/Interim Objectives represent an essential guide for the protection and maintenance of water quality and may form the basis of chemical-specific effluent limits.

Thallium was identified in the Effluent Monitoring Priority Pollutant List (EMPPL) as a chemical of potential environmental concern due to its toxicity and presence in effluents discharged to surface waters of Ontario.

The purpose of this document is to derive a Provincial Water Quality Objective (PWQO) wherever possible, using at least a minimum required amount of toxicological information. Where fewer data exist, an Interim Provincial Water Quality Objective (IPWQO) is developed.

1.1 Sources and Uses

Thallium (Tl) is an inorganic element that is present in the earth's crust at concentrations that range from 0.3 to 0.6 mg/kg (NRCC 1982). Thallium is rarely present as large ore deposits but can be recovered from sulphide ores of lead, copper, and zinc. Thallium may also be associated with cadmium, iron ores and potassium minerals such as feldspars and micas. Thallium minerals occur naturally but are rare; they include crookesite, hutchinsonite, lorandite and avicennite.

Thallium may be recovered by metal electrolysis, precipitation and reduction during the mining and smelting of other ores. Most of the thallium used in Canada is imported from the United States. The element is used in the manufacture of alloys and in the production of electrodes and low melting glass. Thallium sulphate has been used extensively in the past in insecticides and rodenticides but its high, non-selective toxicity has precluded this use. It was deregistered in the USA in 1972 but is still used elsewhere (Wallwork-Barber *et al.* 1985). Currently, there are no pesticides containing thallium registered for use in Ontario

(L. Radzius, OMOEE, Standards Development Branch, pers. comm.). Thallium sulphide is used in photocells; thallium bromide with iodide crystals is used in infrared detectors, and thallium oxide (Tl_2O_3) is a major component of glass of a high index of refraction. Thallium is not a normal constituent of animal or plant cells but has been used medicinally to treat ringworm and skin infections. Thallous acetate was used for measuring ozone and thallium chloride is used in sun-tan lamp monitors. Thallium nitrate has pyrotechnical applications. Its green flame, when burned, gave rise to its name: thallos - greek for new shoot. Emsley (1991) estimated that world production of thallium was approximately 30 tonnes/yr for 1985.

Thallium enters aquatic environments naturally when it is released from bedrock by weathering processes. Natural inputs of thallium to aquatic systems are not toxicologically significant. However, anthropogenic point sources which include potash, industrial effluents from roasting of pyrite during the production of sulphuric acid, and mining and smelting of copper, gold, zinc, lead and cadmium (McNeely *et al.* 1979), are a potential concern. Combustion of coal and oil also releases thallium as a component of fly ash emissions from power plants (NRCC 1982) and is a potential source of aerial deposition to surface waters.

Recent effluent discharge data are available from Ontario's Municipal/Industrial Strategy for Abatement (MISA) monitoring reports. Ten industrial sectors (iron and steel, organic chemical manufacturing, pulp and paper, metal mining, metal casting, industrial minerals, inorganic chemicals, petroleum, waste water treatment plants and hydro-electric generation) were required to monitor effluent quality for a one year period (OMOE 1988, 1990, 1991a-f, 1992a, Ramchandani, pers. comm.). Quantification of the total mass loadings (effluent flow X effluent concentration) of thallium discharged to Ontario's surface waters is very unreliable due to low sample numbers, treatment of data below the regulatory detection limit, and general lack of intake concentrations. Aerial deposition onto surface waters is a potential source near combustion sources, especially of coal and oil, but the importance of this in Ontario is unknown.

1.2 Properties and Fate

The physical-chemical properties of thallium and selected thallium compounds are presented in Table 1.

Thallium exists in aquatic systems in oxidation states of +1 and +3. The thallous ion, Tl(I), does not complex readily, whereas, the thallic ion, Tl(III), is present in several organometallic compounds (Cotton and Wilkinson 1980).

The behaviour of thallium in aquatic systems is not well described but has been summarized by CCREM (1987). Generally, thallium may (1) be removed from the water column through adsorption to sediments and suspended particulates which eventually settle, (2) remain in solution as soluble complexes or (3) be absorbed and bioaccumulated by organisms. The chemical form and behaviour of thallium may be influenced by pH, temperature, concentration of dissolved oxygen, presence of humic acid and ligands (CCREM 1987). In natural aerobic waters, the predominant form is the thallous ion. In reducing environments thallium may be precipitated in the presence of sulphur as the insoluble sulphide (Lee 1971, Magorian *et al.* 1974). Soluble thallic compounds may also be precipitated when hydrolysed to form colloidal oxides. Thallium does not readily complex with humic acids and the interactions of ligands and thallium are affected by pH. O'Shea and Mancy (1978) found that significant binding with humates occurred only above pH 7.2. Conversely, as pH increases from 6.2 to 9.1, thallium-inorganic interactions decrease. Thallium adsorbed strongly to montmorillonite clay at pH 8.1, whereas sorption was not extensive at pH 4 (Magorian *et al.* 1974).

Wallwork-Barber *et al.* (1985) studied the behaviour of thallium in freshwater microcosms. They observed compartmentalization of thallium into water, sand, vegetation and fish. The concentration of thallium declined in the water column following first-order kinetics, increased in the fish and vegetation and remained at similar levels in the sandy sediments.

Biomethylation of thallium has been demonstrated in anaerobic bacterial cultures where Tl (III) was methylated to form $(CH_3)_2Tl^+$ (Huber *et al.* 1978), but the extent to which this occurs under natural conditions is unknown (NRCC 1982).

1.3 Detection Limits and Ambient Concentrations

The present Ontario Ministry of Environment and Energy detection and quantification limits in water for thallium are 0.01 and 0.1 mg/L, respectively. Instrument detection limits

for thallium using ICP, graphite furnace and ICP-MS have been reported to be 0.05, 0.005 and 0.0001 mg/L, respectively (Boomer, pers. comm.).

Data on the ambient concentrations of thallium in various environmental media are sparse. Ambient levels (not necessarily background) of thallium ranged from 0.1 to 0.8 mg/kg (soils), 0.07 to 6.0 mg/kg (urban dust), 0.03 to 0.3 mg/kg (vascular plants) and 0.08 mg/kg in fish soft tissue, (CCREM 1987). Concentrations in surface fresh waters ranged from 0.0052 to 0.1 mg/L in the Pacific region of Canada. The detection limit was 0.005 mg/L (NAQUADAT 1985). The OMOEE Drinking Water Surveillance Program reported raw water intake data for 1992 and 1993. Nine of 101 sites reported a few samples with Tl above the detection limit of 0.05 mg/L. Maximum concentrations ranged from 0.06 to 0.1 mg/L (H. Graham, Environmental Monitoring & Reporting Branch, OMOEE, Toronto, pers. comm.). Thallium concentrations in surface waters of a catchment basin to mining industries ranged from 0.001 to 0.080 mg/L (Zitko *et al.* 1975). Calspun Corporation (1977) reported thallium sediment concentrations of 5 mg/kg downstream of copper and zinc industries. Concentrations of thallium in Wintergreen Lake (Kalamazoo, MI), where contamination with coal flyash had occurred, ranged from 2.1 to 23.1 mg/L (Mathis and Kevern 1975). There are no good recent determinations of open water (i.e. background) thallium concentrations using newer "clean room" research methodologies.

2.0 TOXICITY

Thallium is highly toxic to plants and animals and there are several documented human poisonings, primarily arising from the misuse of pesticides containing thallium. Mammals are more sensitive to thallium than to cadmium, lead, copper or zinc; only methyl mercury is more toxic. Chronic thallium exposure in humans may produce optic atrophy (wasting of eye tissues) and altered pupillary reflexes, paraesthesia (burning or tingling sensation), and changes in superficial tendon reflexes. Acute poisonings result in gastrointestinal symptoms, abdominal colic (spasms or pains), loss of kidney function, peripheral neuritis (nerve inflammation), strabismus (squinting), disorientation, convulsions. Joint pain and alopecia (hair loss) develop rapidly. Death is due to damage to the central nervous system (Sittig 1985). Thallium toxicity results in damage to ventral horn cells and dorsal root ganglion cells as well as to dorsal columns in the spinal cord. Secondary degeneration of the axons and

damage to the myelin sheaths also occurs (Norton 1980). In plants, thallium strongly inhibits influx of Cl^-, SO_4^{2-} and HCO_3^- at 5 x 10^{-5} and 5 x 10^{-3} M *in vitro* (10.22 and 1022 mg/L, respectively) (Metlička and Rybová 1983). Thallium (I) is isomorphic with potassium but has a much higher (10x) affinity for enzymes and therefore thallium(I) can substitute for monovalent cations (see Zitko 1975). There are few data regarding toxicity of thallium to aquatic organisms. Available toxicity data are summarized in Table 2 and are current to May 1993.

2.1 Acute Toxicity to Aquatic Organisms[1]

2.1.1 Vertebrates

Zitko *et al.* (1975) continuously exposed juvenile Atlantic salmon (*Salmo salar*), 7.6 to 13.8 cm in length, to measured concentrations of thallium in soft water with a hardness of 14 mg/L. The 96-h LC50 value of ≈1.4 mg/L was interpolated from an equation for the toxicity curve (log time to 50% mortality versus log thallium concentration). Zitko *et al.* (1975) concluded that thallium is less acutely toxic to fish than the other metals but a greater hazard at low concentrations and longer exposure durations. It is noteworthy that Zitko *et al.* (1975) found that in binary mixtures of thallium and either zinc or copper the toxicity of either metal was unaffected by the presence of the other (independent toxicity). Further, they speculated that based on chemical properties, neither humic acids (i.e. dissolved organic carbon) nor hardness would have much effect on thallium toxicity. Nehring (1962, translated from German) found acute toxicity values of thallium nitrate to rainbow trout, perch and roach that were substantially higher (less toxic) than those of Zitko *et al.* (1975) (Table 2). After three days of exposure rainbow trout fingerlings, sub-adult perch and roach began to die at 10-15, 60 and 40-60 mg/L, respectively (Nehring 1962), but 2 mg/L caused no mortality in trout or roach in 17-d exposures.

LeBlanc and Dean (1984) reported a preliminary 96-h LC50 value of 0.860 mg/L for early lifestages of fathead minnows exposed to thallium sulphate, but gave few experimental details.

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[1] Distinctions of acute/chronic and primary/secondary data classifications are outlined below in section 6.

Buccafusco *et al.* (1981) determined the 96-h LC50 for bluegill sunfish (*Lepomis macrochirus*) exposed to thallous sulphate to be 120 mg/L. The exposure concentrations were not measured. Dawson *et al.* (1977) also exposed bluegill sunfish, 33 to 77 mm in length, to concentrations ranging from 32 to 320 mg/L of thallium in the form of thallium acetate, for 96 h. The 96-h LC50 value was 132 mg/L.

Kimball (undated report) conducted acute tests lasting up to 8 d using 12-16 mm, 8 week-old fathead minnows under continuous flow conditions with measured concentrations. The resulting 4-d and 8-d LC50s were 1.8 and 1.45 mg/L respectively.

2.1.2 Invertebrates

Kimball (undated report) conducted acute tests with *Daphnia magna*. Tests used neonates <24-h old and were static, lasting either 48 h with and without feeding, or 96 h with feeding. Feeding had no effect, and the 48-h LC50s averaged 0.91 mg/L. The 96-h LC50 was 0.68 mg/L. These data were considered primary.

Secondary acute toxicity data for thallium and thallium compounds were also available for *Daphnia* sp. and *Gammarus* sp. Nehring (1962) reported that concentrations of 2 to 4 mg/L of thallium nitrate caused complete mortality (LC100) in both of these species (Table 2). The 48-h LC50 estimate for neonate *Daphnia magna* exposed to thallium under static conditions was 2.2 mg/L (LeBlanc 1980). The values ranged from 1.9 to 2.6 and the acute NOEC for Tl was 1.7 mg Tl/L.

2.2 Chronic Toxicity to Aquatic Organisms

2.2.1 Vertebrates

LeBlanc and Dean (1984) exposed fertilized eggs and larvae of the fathead minnow (*Pimephales promelas*) to thallium sulphate in well water using a Mount-Brungs continuous flow proportional diluter. The pH, concentration of dissolved oxygen, temperature and concentrations of thallium were measured daily and/or weekly. Embryos were less sensitive

to thallium than the larvae. A thallium concentration of 0.72 mg/L killed all of the embryos, whereas 0.35 mg/L significantly reduced % hatch and 0.2 mg/L had no effect. By 30-d post-hatch, 0.35 mg/L had killed all larvae and 0.04 mg/L (the lowest test concentration) significantly reduced survival. Length and weight were less sensitive responses, being significantly reduced at 0.12 and 0.2 mg/L, respectively. Therefore, the lowest observable effect concentration (LOEC) was 0.04 mg/L. LeBlanc and Dean (1984) divided the 96-h LC50 estimate by the LOEC (0.86/0.04 mg/L) to get an ACR (acute to chronic ratio) of 21.5. The authors actually state the MATC (geometric mean of the LOEC and NOEC) is < 40 µg/L, since they had no NOEC values. This gives an ACR of >22. The authors went on to conclude that the ACR indicated potential for chronic toxicity although less than that for lead, nickel or cadmium.

Chronic toxicity of thallium to fathead minnows was tested by Kimball (undated report) starting with eggs <40-h old and lasting until 28 days post hatch. Thallium was noteworthy in that it produced a high percentage (68%) of abnormal fry at hatch. At 28 d, survival was only 45% at 0.292 mg/L, but length was the most sensitive endpoint. Fish exposed to 0.081 mg/L were significantly shorter than controls.

Birge (1978) evaluated the toxicity of thallium to embryos of three different species. For embryos of the toad (*Gastrophryne carolinensis*) estimated the 7-d LC50 values were 0.11 mg/L. The 7-d LC50 estimate for goldfish embryos *(Carassius auratus)*, was 7 mg/L. In rainbow trout colder temperatures required a 28-d exposure spanning fertilization to 4d post-hatch. This resulted in an LC50 estimate of 0.17 mg/L. These data were considered primary.

All other studies were considered secondary. An early study on the chronic effects of thallium on the "germination" of frogs' spawn and on the growth of tadpoles showed thallium to be toxic at concentrations of 0.4 mg/L (Dilling and Healey 1926). These data were considered to be secondary because concentrations of thallium were not measured.

Compared to some other better-studied metals (e.g. copper or zinc), thallium has been observed to kill fish more slowly, at concentrations ranging from 10 to 60 mg/L (Zitko *et al.* 1975; Nehring 1962). Zitko *et al.* (1975) exposed juvenile Atlantic salmon to thallium concentrations that ranged from 0.20 to 10 mg/L. Mortality was 100% after 108 d in seven of the nine test concentrations. The two lowest concentrations resulted in 40% mortality

(same as controls, hence the classification as secondary) and 70% mortality, respectively. An incipient lethal level (ILL) of 0.03 mg/L was interpolated from the toxicity curve (LT50 versus the log thallium concentration) even though there was no clear threshold. Zitko *et al.* (1975) stated, on the basis of an ILL of 0.03 mg/L, that thallium toxicity was three to four times more "acutely" toxic on a molar basis to Atlantic salmon than copper (i.e. they considered these tests to be acute because they dealt with lethality as opposed to reproduction or growth).

2.2.2 Invertebrates

Only one primary and one secondary chronic study was found using invertebrates. Chronic toxicity of thallium to *Daphnia magna* was tested by Kimball (undated report). Tests were static with replacement and survival and several indices of reproductive success were measured. The 28-d LC50 was 0.393 mg/L Tl, but number of young produced declined significantly at 0.181 mg/L.

2.2.3 Other Organisms (Protozoa, Algae/Plants, Bacteria)

The population growth of the protozoan, *Paramecium bursaria*, was significantly affected at concentrations of 9 mg/L. This study was carried out using a broth solution. It is not known whether the constituents of this broth had any affect on toxicity (DiGaudio 1975).

Algae were adversely affected at 0.100 mg/L (USEPA 1980). Den Dooren De Jong (1965) evaluated the tolerance of *Chlorella vulgaris* to metallic ions. A chronic exposure of 3 to 4 months in growth media containing thallium sulphate yielded two endpoints. The highest concentration tolerated was 0.00002 g atoms/L (4.1 mg Tl/L) and the lowest inhibitory concentration was 0.00004 g atoms/L (8.2 mg Tl/L). These data are of poor quality and are hence classified as ancillary and not used for objective development.

Overnell (1975) exposed whole cells and cell fragments of *Chlamydomonas reinhardtii* to thallium. Thallium inhibited light-induced oxygen evolution by blocking either the reduction of NADP or enzyme systems of the dark reaction in photosynthesis (Table 2).

Brown and Rattigan (1979) exposed rooted, actively growing *Elodea canadensis* and free floating duckweed (*Lemna minor*) to thallium sulphate for 28 d and 14 d respectively, and visually scored damage in whole plants. The 28-d EC50 estimate was 2.0 mg/L for *Elodea* while the 14-d EC50 was 0.008 mg/L for *Lemna minor*. The plants were grown in a dilute medium containing major ions and HEPES buffer. This buffer has negligible metal complexing capacity. Test concentrations of thallium in the study were not reported.

Brown and Rattigan (1979) collected sprigs of *Elodea canadensis* in the field. In the laboratory the sprigs were removed and cut into short segments and exposed to thallium for 24 h. The rate of photosynthesis, expressed as the oxygen evolution rate relative to plant material in the control treatments, was then measured on one gram samples. The 24-h IC50 estimate (the thallium concentration that reduced the O_2 evolution rate to 50% of that in the untreated control plant material) for *Elodea canadensis* exposed to thallium sulphate was 1.43 mg/L. The 24-h IC90 was 2.75 mg/L.

DiGaudio (1975) reported that a concentration of 3 mg/L of thallium resulted in significant growth inhibition of both *Anacystis nidulans* and *Chlorella vulgaris*. Both tests were carried out using a broth solution. It is not known whether the constituents of this broth had any affect on toxicity.

Smith and Kwan (1989) exposed duckweed (*Lemna minor*) to thallium for ten days and measured growth rate and frond production. They reported that the EC50 for frond production was 0.2 nmol/mL (0.04 mg/L). An earlier paper (Kwan and Smith 1988) reported 10d-EC50s of 0.03 mg/L, 0.04 mg/L and 0.05 mg/L for decreases in frond area, frond weight and frond number, respectively.

2.3 Summary of Toxicity Data to Aquatic Organisms

2.3.1 Acute

Acute toxicity estimates for fish exposed to thallium were between 0.86 and 132 mg/L (Table 2). The most sensitive aquatic animal to acute thallium exposures was the fathead minnow.

2.3.2 Chronic

There were three studies that produced primary chronic data for four aquatic vertebrates. Thallium was chronically toxic to fathead minnows, goldfish, rainbow trout and narrow-mouth toads at 0.04 to 1.2 mg/L, 7 mg/L, 0.17 mg/L and 0.11 mg/L, respectively (LeBlanc and Dean 1984, Birge 1978, Kimball undated report). The remaining studies were considered secondary data because thallium concentrations were not measured or details regarding testing procedures were insufficient.

There was one primary chronic toxicity study for aquatic invertebrates. Kimball (undated report) reported three endpoints for studies with *Daphnia magna*. The lowest was a lifecycle reproductive effect at 0.181 mg/L. One secondary chronic study was available for a protozoan (DiGaudio 1975).

Secondary data were available for six plant species (Table 2). The most sensitive indicator species of thallium toxicity is the common duckweed, *Lemna minor,* which had a 14-d EC50 (plant damage) value of 0.008 mg/L. Macrophytes were more tolerant with 28-d EC50 values of 2.0 mg/L, but the endpoints were subjective (Brown and Rattigan 1979).

Overall, toxic responses to waterborne thallium in the laboratory spanned over four orders of magnitude - from 0.01 mg/L to 200 mg/L. The frequency distribution for the forty-seven tests is shown in Figure 1. Ranges are shown for vertebrates, invertebrates and plants for interest. However, no inferences about relative sensitivities should be drawn from the figure since these cover a variety of endpoints and exposure situations.

3.0 BIOACCUMULATION

Thallium bioaccumulates only slightly in aquatic organisms. Molluscs continuously exposed to Tl for 88 d at 0.05 and 0.1 mg/L accumulated 3.7 and 10.78 µg/kg dry weight (d.w.) respectively. Forty day exposures to thallium resulted in 2.17 and 5.29 µg/kg d.w. (Oehme 1979). Assuming a 75% water content, this would indicate a bioconcentration factor (BCF) of much less than one.

Kwan and Smith (1988) reported that thallium was highly bioaccumulative in the duckweed, *Lemna minor*. BCFs ranged from 6000 to 88000, dependent upon water concentrations. In a later paper (Smith and Kwan 1989) they reported that at an exposure concentration of 0.2 nmol/ml (0.04 mg/L), thallium reached a steady state in duckweed, after approximately 140 h. The calculated BCF was 7000. They also reported that depuration occurred rapidly over the first three hours of exposure, but after 48 hours, no further depuration occurred. In attempting to determine the uptake kinetics of thallium by the duckweed, Kwan and Smith (1991) found that Ca^{2+} and K^{+} antagonists did not shed any light on the modes of entry of thallium into the plant. However, they did hypothesize that thallium may be held in cell vacuoles as retention of thallium occurred even when the plants were moved to clean water. They further concluded that thallium uptake was an active process and the ion activity of thallium was unaffected by changes in pH and ligand concentration.

Barrows *et al.* (1980) measured the bioconcentration of thallous sulphate (Tl_2SO_4) by bluegill sunfish (*Lepomis macrochirus*) which weighed between 0.37 and 0.94 g and were 25 to 32 mm long. The fish were collected in the field and allowed to acclimate for 30 d in the laboratory. A modified Mount and Brungs continuous-flow, proportional diluter was used to expose the fish to thallium in well water. The exposure period was 28 d, temperature 16 ± 1°C, pH 7.1, hardness 35 mg/L as $CaCO_3$, and the dissolved oxygen concentration ranged between 5.9 and 8.6 mg/L. The concentration of thallium in the water averaged 0.080 ± 0.010 mg/L. The maximum bioconcentration factor was 34; however, the half-life in fish was greater than four days, and exceeded the seven day depuration period. Therefore, despite the relatively low BCF, it remained in the body for substantially longer than 27 other compounds tested (Barrows *et al.* 1980). Laboratory exposures up to 200 µg/L over 300 h resulted in BCFs of 114-130 in muscle, 80-235 in liver and 27-1430 in gill, respectively (Zitko *et al.* 1975). BCFs exceeded 1000 only in gill tissue, and then only at the lowest exposure concentration of 0.018 µg/L.

4.0 ODOUR AND TASTE

No data were found concerning the taste or odour effects of thallium or thallium compounds on the quality of water or biota destined for human consumption.

5.0 MUTAGENICITY

Mutagenicity refers to permanent and heritable changes to genetic material.

A review of the mutagenicity literature available for thallium was done on-line through the IRIS database (IRIS 1993). Studies reported that thallium (I) salts were not mutagenic in reverse mutation assays using *Salmonella typhimurium* (Ames test) and *E. coli*.

Three studies were reported for thallium nitrate. A positive genotoxic response was reported for a REC assay which exposed *Bacillus subtilis* to 0.01M thallium nitrate. However, negative responses were reported when testing for cell division in yeast and *E. coli*, and for induction of mitotic gene conversions and reverse mutation in yeast. The one positive response may be attributed to nitrification as opposed to the presence of thallium.

Two positive responses in assays using mammalian tissue culture cells were reported for thallium carbonate. Single strand chromosome breaks in mouse and rat embryo fibroblasts at concentrations of 10^{-6} and 10^{-4}M were reported. These studies indicate that thallium may cause chromosomal damage.

A positive study was obtained for a virally enhanced, cell transformation of Syrian hamster embryo (SHE) cells using thallium acetate. A positive response was also reported for a similar study using thallium chloride.

Thallium has been reported to be a teratogen in experimental animals (Emsley 1991). A teratogenic response to thallium salts characterized as achondroplasia (dwarfism) has been described in rats (Nogami and Terahima 1973).

IRIS lists a positive response in an *in vivo* dominant lethal study with male white mice.

In a review paper, Sharma and Talukder (1987) reported that thallium has been shown to clastogenically (chromosomal breaks) effect both the chromosomes and the spindles of plants, as well as mammalian bone marrow *in vivo*. Thallium salts may affect spindle fibres which effect chromosomal separation at cell division.

In summary, thallium salts should be considered genotoxic, likely causing chromosomal damage in mammalian and plant cells. However, no data were found which reported genotoxic effects on aquatic organisms. Therefore, a numeric Interim Objective to protect aquatic organisms against mutagenic effects of thallium could not be derived. The USEPA reports that there was insufficient evidence to classify thallium as a human carcinogen, nor is there evidence to suggest that thallium is a mutagen. However, there is some evidence to suggest that it may be a teratogen. Furthermore, there are a number of studies indicating that thallium is a clastogen. Therefore, exposure to thallium may result in genotoxic effects in aquatic organisms. The derived IPWQO for thallium may not protect against these effects.

6.0 DERIVATION OF INTERIM PROVINCIAL WATER QUALITY OBJECTIVE

For the purposes of criteria development, toxicity data are classified by OMOEE as primary or secondary, acute or chronic. All candidate toxicological information is screened for acceptability. To be considered primary, the following must apply: accepted laboratory practices of exposure and environmental controls; stable, measured concentrations of toxicant throughout the test; test endpoints and lengths of exposure appropriate to the life stage of the species tested and the characteristics of the substance; relevant environmental parameters such as temperature, pH and hardness must have been recorded; responses and survival of controls must be appropriate for the species and test used. Data on vertebrates and invertebrates not meeting all of the above are denoted as secondary in objective development documents.

The words acute and chronic in connection with toxicity tests refer to short (acute) and long (chronic) exposure. Such terms require a specific organism as a reference. For a *Daphnia* with a life cycle of weeks, acute usually means two days or less. However, for trout with a life cycle of years, acute usually means four days or less. When classifying test results for a substance as either acute or chronic based on the duration of exposure, the nature of the substance and how rapidly it acts is considered. More detail is given in OMOE (1992b).

The minimum data base to develop a Provincial Water Quality Objective was not met for thallium. There was a lack of primary chronic data for only one non-crustacean invertebrate. Therefore an Interim Provincial Water Quality Objective was developed by completing the

Uncertainty Factor Worksheet (Table 3). These procedures are described in more detail in OMOE (1992b). All of the toxicity data are shown on Figures 1 and 2.

6.1 Calculation of Final Uncertainty Factor

The Uncertainty Factor Worksheet (Table 3) uses both acute and chronic data. For each of these up to three different species of fish, and two species of invertebrates from different orders may be used. One piece of algal or aquatic plant data is also permitted. Plant exposures are considered chronic due to their generally shorter life span. The baseline uncertainty factor is then selected - either 1000 or 10000 based on whether the substance is, or has the potential to be, bioaccumulative. The best quality data are chosen from Table 2 - Aquatic Toxicity Data, to give the lowest uncertainty factor. These toxicity data are then given a weighting factor which is used to reduce the baseline uncertainty factor. Finally, the lowest effect endpoint from Table 2 is divided by the final uncertainty factor from Table 3 to give the Interim Provincial Water Quality Objective.

The final uncertainty factor is based on the following information:

6.1.1 Acute

1. The 8-d LC50 estimate of 1.45 mg/L for fathead minnows (Kimball, undated report) was considered to be a primary study.
2. The 96-h LC50 value of 120 mg/L for bluegill sunfish (Buccafusco *et al.* 1981) was considered to be a secondary study.
3. The 96-h LC50 estimate of 1.4 mg/L for exposure of Atlantic salmon (Zitko *et al.* 1975) was obtained from the equation given by the authors and considered to be a secondary study.

4,5. The invertebrate 48-h LC50 estimates of 0.91 and 4 mg/L for *Daphnia magna* (Kimball, undated report) and *Gammarus* sp. (Nehring 1962), respectively, were considered primary and secondary data, respectively.

6.1.2 Chronic

1. The 28-d LC50 estimate of 0.17 mg/L for rainbow trout was considered primary data (Birge 1978).
2. A concentration of 0.081 mg/L resulted in a significant decrease in growth of fathead minnows over 28 days (Kimball, undated report). This study was considered primary data.
3. The 7-d LC50 of 7 mg/L for early life stages of the goldfish (Birge 1978) was considered primary data.
4. The *Daphnia magna* 96-h LC50 estimate of 0.68 mg/L (Kimball, undated report) was considered primary.
5. The *Paramecium* 96-h threshold concentration of 9 mg/L was considered secondary data.
6. The 14-d EC50 value of 0.008 mg/L for *Lemna minor* was the lowest toxicity estimate for plants (Brown and Rattigan 1979 - see Table 4). This is secondary by policy.

The baseline uncertainty factor for inorganics (OMOE 1992b) is 1,000 unless there is evidence for bioaccumulation. Thallium does bioconcentrate in aquatic biota and more highly in plants than animals. The highest calculated BCF for whole body of fish was less than 1,000. Hence, the baseline uncertainty factor for thallium is 1,000. The calibration factors presented in Table 3 resulted in a calculated final uncertainty factor of 24.

6.2 Calculation of the Interim Objective Value

The calculated final uncertainty factor is 24. The lowest measured chronic toxicity value was 0.008 mg/L for *Lemna minor* exposed to thallium (Brown and Rattigan 1979). Therefore, following the procedures (OMOE 1992b), the preliminary IPWQO for thallium is 0.0003 mg/L (0.008 divided by 24). This IPWQO for thallium should protect aquatic plant life since it is lower than the lowest concentration of 0.008 mg/L that adversely affected *Lemna minor*. The value is more stringent than the criteria established by NYSDEC (1987) of 0.008 mg/L to protect fishing and fish propagation (see section 8.0).

The recommended Interim Provincial Water Quality Objective for thallium to protect freshwater aquatic life is 0.0003 mg/L.

7.0 RESEARCH NEEDS

This section summarizes only research required by OMOEE for criteria development. In order to upgrade the Interim Objective to an Objective, one primary chronic toxicity estimate is required for one invertebrate species which is not a crustacean. There is also a requirement for mutagenicity data in aquatic organisms. To reduce the IPWQO uncertainty factor, additional primary acute studies are needed for invertebrates and fish and chronic studies are required for invertebrates. More data on ambient levels in Ontario waters would be useful.

8.0 OBJECTIVES OF OTHER AGENCIES

New York State established an ambient water quality standard to protect fishing and fish propagation of 0.008 mg/L for the acid-soluble form of thallium using chronic toxicity tests (NYSDEC 1987 - see Figure 2). New York State also established a standard to protect fishing and fish survival of 0.020 mg/L using acute toxicity tests (NYSDEC 1987). Unfortunately, NYSDEC (1987) does not provide the rationale or toxicity data to support their standards.

The USEPA (1980) indicated that toxicity of thallium to aquatic life occurred at 1.4 and 0.040 mg/L, for acute and chronic toxicity, respectively, to freshwater aquatic life but did not establish any criteria to protect aquatic life because of insufficient data.

9.0 REFERENCES

Barrows, M.E., S.R. Petrocelli, K.J. Macek and J.J. Carroll. 1980. Bioconcentration and elimination of selected water pollutants by bluegill sunfish (*Lepomis macrochirus*), pp. 379-392. *In* Dynamics, exposure and hazard assessment of toxic chemicals, R. Hague (ed). Ann Arbor Sci.

Birge, W.J. 1978. Aquatic toxicology of trace elements of coal and fly-ash. *In* Energy and environmental stress in aquatic systems, J.H. Thorp and J.W. Gibbons (eds). Department of Energy Symposium Series CONF-771114.

Boomer, D. 1993. Personal Communication. Inorganic Trace Contaminants Section. Laboratory Services Branch. Ontario Ministry of Environment and Energy. Rexdale, Ontario.

Brown, B.T. and B.M. Rattigan. 1979. Toxicity of soluble copper and other metal ions to *Elodea canadensis*. Environ. Pollut. 20:303-314.

Buccafusco, R.J., S.J. Ellis and G.A. LeBlanc. 1981. Acute toxicity of priority pollutants to Bluegill (*Lepomis macrochirus*). Bull. Environ. Contam. Toxicol. 26: 446-452.

Calspun Corporation. 1977. Heavy metal pollution from spillage at ore smelters and mills. Report of the Calspun Corporation, Buffalo, NY, for the US Environmental Protection Agency. Cincinnati, OH.

CCREM. 1987. Canadian Water Quality Guidelines. Prepared by the Task Force on Water Quality Guidelines of the Canadian Council of Resource and Environment Ministers.

Cotton, F.A and G. Wilkinson. 1980. Advanced Inorganic Chemistry. John Wiley and Sons. New York, NY. 1396 p.

Dawson, G.W., A.L. Jennings, D. Drozodowski and E. Rider. 1977. The acute toxicity of 47 industrial chemicals to fresh and saltwater fishes. J. Hazard. Mat. 1: 303-318.

Den Dooren De Jong, L.E. 1965. Tolerance of *Chlorella vulgaris* for metallic and non-metallic ions. J. Microbiol. Ser. 31: 301-313.

DiGaudio, M.R. 1975. Thallium: Some effects of an environmental toxicant. Ph.D. Thesis. New York University, N.Y. 68p.

Dilling, W.J. and C.W. Healey. 1926. Influence of lead and the metallic ions of copper, zinc, thorium, beryllium and thallium on the germination of frogs' spawn and on the growth of tadpoles. Ann. Appl. Biol. 13:177-188.

Emsley, J. 1991. The Elements. Second Edition. Clarendon Press. Oxford, England. 251p.

Huber, F., U. Schmidt and H. Kirchmann. 1978. Aqueous chemistry of organolead and organothallium compounds in the presence of microorganisms. *In* Organometals and Organometalloids: Occurrence and Fate in the Environment. F.E. Brinkman and J.M. Bellama (eds). Am. Chem. Soc. Symp. Ser. No. 82.

IRIS. 1993. Integrated Risk Information System. USEPA. Washington, D.C.

Kimball, G. (undated report). The effects of lesser known metals and one organic to fathead minnows (*Pimephales promelas*) and *Daphnia magna*. Department of Entomology, Fisheries and Wildlife, University of Minnesota.

Kwan, K.H.M. and S. Smith. 1988. The effect of thallium on the growth of *Lemna minor* and plant tissue concentrations in relation to both exposure and toxicity. Environ. Pollut. 52(3):203-219.

Kwan, K.H.M. and S. Smith. 1991. Some aspects of the kinetics of cadmium and thallium uptake by fronds of *Lemna minor* L. New Phytol. 117:91-102.

LeBlanc, G.A. and J.W. Dean. 1984. Antimony and thallium toxicity to embryos and larvae of fathead minnows (*Pimephales promelas*). Bull. Environ. Contam. Toxicol. 32:565-569.

LeBlanc, G.A. 1980. Acute toxicity of priority pollutants to water flea (*Daphnia magna*). Bull. Environ. Contam. Toxicol. 24:684-691.

Lee, A.G. 1971. The Chemistry of Thallium. Elsevier Publ. Co. Amsterdam, Netherlands.

Magorian, T.R., K.G. Wood, J.G. Michalovic, S.L. Pek and M.M. Van Leir. 1974. Water pollution by thallium and related metals. NTIS PB 253 333. Springfield, Virginia. 182 p. (as cited in USEPA 1980).

Mathis, B.J. and N.R. Kevern. 1975. Distribution of mercury, cadmium, lead and thallium in an eutrophic lake. Hydrobiologia 46: 207-222.

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. Thallium. *In* Water Quality Sourcebook. A guide to water quality parameters. Water Quality Branch, Inland Waters Directorate. Environment Canada, Ottawa.

Metlička, R. and R. Rybová. 1983. Effect of Tl^+ ion on membrane potential and resistance in *Hydrodictyon reticulatum.*, pp. 335. *In* Membrane transport in plants. W.J. Cram, K. Janaček, R. Rybova and K. Sigler (*Eds.*). John Wiley and Sons. New York, NY.

NAQUADAT. 1985. National Water Quality Data Bank. Water Quality Branch, Inland Waters Directorate. Environment Canada, Ottawa.

Nehring, D. 1962. Untersuchungen uber die toxikologische Wirkung von Thallium-ionen auf fische und fischnahrtiere. Z. Fischerei 11: 557-561. (as translated from German).

Nogami, H. and Y. Terashima. 1973. Thallium induced achondroplasia in the rat. Teratology, 8:101-102. (from Hammond and Beliles 1980).

Norton, S. 1980. Chapter 9. Toxic Responses of the Central Nervous System. *In* Casarett and Doull's Toxicology. The Basic Science of Poisons. 2nd Edition. Doull, J., C.D. Klaassen and M.O. Amdur (*eds*). Macmillan Publishing Co., Inc. New York, N.Y. pp179-205.

NRCC. 1982. Data sheets on selected toxic elements. Associate Committee on Scientific Criteria for Environmental Quality. National Research Council of Canada, Ottawa.

NYSDEC. 1987. New York State Ambient Water Quality Standards and Guidance Values. New York State Department of Environmental Conservation, Albany, New York. 37 pp.

Oehme, F. 1979. Toxicity of heavy metals in the environment, Part 2. Marcel Dekker, Inc. New York, NY. 970 p.

OMOE. 1988. Thirty Seven Municipal Water Pollution Control Plants. Pilot Monitoring Study. Volume 1. Interim Report. Municipal/Industrial Strategy for Abatement. Water Resources Branch. Ontario Ministry of the Environment.

OMOE. 1990. Second Report on the Monitoring Data for the Petroleum Refining Sector. Municipal/Industrial Strategy for Abatement. Water Resources Branch. Ontario Ministry of the Environment.

OMOE. 1991a. Status Report: The Metal Mining Sector Effluent Monitoring Data. For the period February 1, 1990 to January 31, 1991. Municipal/Industrial Strategy for Abatement. Water Resources Branch. Ontario Ministry of the Environment.

OMOE. 1991b. Preliminary Report on the First Six Months of Process Effluent Monitoring in the MISA Pulp and Paper Sector (January 1, 1990 to June 30, 1990). Municipal/Industrial Strategy for Abatement. Water Resources Branch. Ontario Ministry of the Environment.

OMOE. 1991c. Status Report on the Effluent Monitoring Data for the Iron and Steel Sector for the Period from November 1, 1989 to October 31, 1990. Municipal/Industrial Strategy for Abatement. Water Resources Branch. Ontario Ministry of the Environment.

OMOE. 1991d. Effluent Monitoring Data for the Organic Chemical Manufacturing Sector (Draft). Municipal/Industrial Strategy for Abatement. Water Resources Branch. Ontario Ministry of the Environment.

OMOE. 1991e. Effluent Monitoring Data for the Inorganic Chemical Manufacturing Sector (Draft). Municipal/Industrial Strategy for Abatement. Water Resources Branch. Ontario Ministry of the Environment.

OMOE. 1991f. Effluent Monitoring Data for the Metal Casting Sector (Draft). Municipal/Industrial Strategy for Abatement. Water Resources Branch. Ontario Ministry of the Environment.

OMOE. 1992a. Twelve Month Monitoring Data Report Industrial Minerals Sector for the Periods February 1, 1990 to January 31, 1991 and August 1, 1990 to July 31, 1991. Municipal/Industrial Strategy for Abatement. Water Resources Branch. Ontario Ministry of the Environment.

OMOE. 1992b. Ontario's Water Quality Objective Development Process. Aquatic Criteria Development Committee. Water Resources Branch. Ontario Ministry of the Environment.

OMOEE. 1994. Water Management: Policies, Guidelines, Provincial Water Quality Objectives of the Ministry of Environment and Energy. Ontario Ministry of Environment and Energy. 53p

O'Shea, T.A. and K.H. Mancy. 1978. The effect of pH and hardness metal ions on the competitive interaction between trace metal ions and inorganic and organic complexing agents found in natural waters. Water Res. 12: 703-711.

Overnell, J. 1975. The effect of some heavy metal ions on photosynthesis in a freshwater alga. Pest. Biochem. Physiol. 5: 19-26.

Radzius, L. pers. comm. Assistant Environmental Scientist. Pesticides Section. Hazardous Contaminants Branch, Ontario Ministry of the Environment. 2 St. Clair Ave. W. Toronto, Ontario.

Ramchandani, C. pers. comm. Sector Specialist - Hydro. MISA. Water Resources Branch, Ontario Ministry of the Environment. 40 St. Clair Ave. W. Toronto, Ontario.

Sax, N.I. and R.J. Lewis, Sr. [eds]. 1987. Hawley's condensed chemical dictionary, 11th ed. Van Nostrand Reinhold Company. New York, NY.

Sax, N.I. and R.J. Lewis, Sr. 1989. Dangerous Properties of Industrial Materials, 7th ed. Van Nostrand Reinhold Company. New York, NY.

Sharma A. and G. Talukder. 1987. Effects of metals on chromosomes of higher organisms. Environ. Mutagen. 9(2):191-226.

Sittig, M. 1985. Handbook of Toxic and Hazardous Chemicals and Carcinogens. 2nd Edition. Noyes Publications. Park Ridge, New Jersey. 950p.

Smith, S. and M.K.H. Kwan. 1989. Use of aquatic macrophytes as a bioassay method to assess relative toxicity, uptake kinetics and accumulated forms of trace metals. Hydrobiologia 188/189:345-351.

USEPA. 1980. Ambient water quality criteria for thallium. Office of Water Regulations and Standards. United States Environmental Protection Agency, EPA 440/5-80-074.

Wallwork-Barber, M.K., K. Lyall and R.W. Ferenbaugh. 1985. Thallium movement in a simple aquatic ecosystem. J. Environ. Sci. Health 6:689-700.

Weast, R.C., M.J. Astle and W.H. Beyer. 1986-1987. CRC Handbook of chemistry and physics. CRC Press, Inc. Boca Raton, FL.

Windholz, M., S. Budavari, R.F. Blumetti and E.S. Otterbein (eds). 1983. The Merck Index, 10th ed. Merck and Co., Inc. Rahway, NJ.

Zitko, V., W.V. Carson and W.G. Carson. 1975. Thallium: occurrence in the environment and toxicity to fish. Bull. Environ. Contam. Toxicol. 13: 23-30.

Zitko, V. 1975. Chemistry, applications, toxicity, and pollution potential of thallium. Fisheries and Marine Services Technical Report No. 518. Environment Canada, Ottawa. 41 p.

Table 1. Physical-Chemical Properties of Thallium and Thallium Compounds.

Chemical Name and CAS No.	Molecular Formula	Melting Point (°C)	Boiling Point(°C)	Molecular Weight (g/mol)	Liquid Density (g/mL)	Vapour Pressure	Solubility	References
Thallium 7440-28-0	Tl	303.5	1457	204.37	11.85 @ 20°C	1 mm @ 825°C	insoluble in H_2O	Sax & Lewis (1989) Windholz et al (1983)
Thallium (I) nitrate (Thallous nitrate) 10102-45-1	$TlNO_3$	206	430	266.38	5.55	n/a	soluble	Sax & Lewis (1989) Windholz et al. (1983)
Thallium(III) nitrate n/a	$Tl(NO)_3$	n/a	n/a	390.40	n/a	n/a	soluble	Weast et al. (1987)
Thallium nitrite n/a	$TlNO_2$	182	n/a	250.39	n/a	n/a	32.1 g/100 cc @ 25°C; 95.78 g/100 cc @ 96°C	Weast et al (1987)
Thallous oxide 1314-32-5	Tl_2O	300	1080	424.77	9.52 @ 16°C	n/a	decomposes in H_2O	Sax & Lewis (1987) Weast et al. (1987)
Thallium(III) oxide (Thallic oxide) 1314-32-5	Tl_2O_3	717 ± 5	decomposes @ 875	456.74	(amorphous) 9.65 @ 21°C (hexagonal) 10.19 @ 22°C	n/a	insol. in cold and hot H_2O	Sax & Lewis (1989) Weast et al. (1987)
Thallium (I) sulfate (2:1) 7446-18-6	Tl_2SO_4	632	n/a	504.80	6.77	n/a	soluble in H_2O	Sax & Lewis (1987) Sax & Lewis (1989)
Thallium (III) sulfate n/a	$Tl_2(SO_4)_3.7H_2O$	loses water at @ 220	n/a	823.05	n/a	n/a	decomposes in H_2O	Weast et al (1987)

TABLE 2: AQUATIC TOXICITY DATA TABLE FOR THALLIUM

SPECIES	LIFE STAGE	RESPONSE	TEST CONDITIONS pH	TEMP (°C)	DO (mg/L)	ALK. (mg/L)	HARD. (mg/L)	EFFECT CONC. (mg/L)	DATA CODES KEY(1)	DATA REF KEY(3)	DATA QUALITY KEY(2)
VERTEBRATES											
Salmo salar	7.6-13.8 cm	108-d ILL[1]	-	7-17.5	-	-	14	0.03	F M	1	S C
(Atlantic salmon)	fry	96-h LC50	-	-	-	-	14	≈1.4	F M	1	S A
Oncorhynchus mykiss											
(Rainbow trout)	6 cm/fry	72-h LC100	7.6-7.9	17	-	150	-	10-15	S U	2	S A
	embryo/larva	28-d LC50	7.4	13	sat.	150	104	0.17	R M	6	P C
	fry	14-d mortality				150		4	S U	2	S C
Perca fluviatilis	12-16 cm	72-h LC100	7.6-7.9	17	-	150	-	60	S U	2	S A
(Perch)		17-d mortality	7.6-7.9	17	-	150	-	15	S U	2	S C
Rutilus spp.											
(Roach)	16-20 cm	72-h LC100	7.6-7.9	17	-	150	-	40-60	S U	2	S A
		8-d mortality						4	S U	2	S C
Pimephales promelas	embryo	96-h LC50	-	-	-		28-40	0.86	NP	3	S A
(Fathead minnow)	embryo/larva	30-d LOEC[2]	6.7-7.2	25±1	8.4	-	28-40	0.04	F M	3	P C
	embryo	no hatch	6.7-7.2	25±1	8.4	-	28-40	0.72	F M	3	P C
	larva	30-d LC100	6.7-7.2	25±1	8.4	-	28-40	0.35	F M	3	P C
	12-16 mm	4-d LC50	7.0	24.5	6-7	~240	"hard"	1.8	F M	12	P A
	8 wk old	8-d LC50	7.0	24.5	6-7	~240	"hard"	1.45	F M	12	P A
	day old	68% abnormal at hatching	7-8	24	-	240	-	1.2	F M	12	P C
	day old	45% survival at d 28 (LOEC)	7-8	24	-	240	-	0.292	F M	12	P C
	day old	28-d posthatch growth	7-8	24	-	240	-	0.081	F M	12	P C
Carassius auratus	embryo	7-d LC50	7.4	22	sat.	-	195	7	R M	6	P C
(Goldfish)											
Lepomis macrochirus	2-5 g	96-h LC50	7.6-7.9	20	-	-	55	132	S U	8	S A
(Bluegill)	0.32-1.2 g	96-h LC50	6.7-7.8	22±1	7-8.8	28-34	32-48	120	S U	10	S A

TABLE 2: AQUATIC TOXICITY DATA TABLE FOR THALLIUM .....Continued

SPECIES	LIFE STAGE	RESPONSE	TEST CONDITIONS pH	TEMP (°C)	DO (mg/L)	ALK. (mg/L)	HARD. (mg/L)	EFFECT CONC. (mg/L)	DATA CODES KEY(1)	DATA REF KEY(3)	DATA QUALITY KEY(2)
Frog (sp. unknown)	tadpole	-	-	-	-	-	-	0.4	R U	5	S C
Gastrophryne carolinensis	embryo	7-d LC50	7.4	22	sat.	-	195	0.11	R M	6	P C
INVERTEBRATES											
Gammarus sp		48-h LC100	7.6-7.9	17	-	-	-	4	S U	2	S A
Daphnia sp		48-h LC100	7.6-7.9	17	-	-	-	2-4	S U	2	S A
Daphnia magna	<24 h	48-h LC50	8.5	20	6.3	230	"hard"	0.91	S M	12	P A
Daphnia magna	<24 h	96-h LC50	8.5	20	6.3	230	"hard"	0.68	S M	12	P C
Daphnia magna	<24 h	48-h LC50	-	-	-	-	-	2.2	S U	11	S A
Daphnia magna	<24 h	48-h NOEC[2]	-	-	-	-	-	1.7	S U	11	S A
Daphnia magna	<24 h	lifecycle reproduction	8.5	20	6.3	230	"hard"	0.181	R M	12	P C
		28-d LC50	8.5	20	6.3	230	"hard"	0.393	R M	12	P C
Paramecium bursaria		96-h TC[11]	-	-	-	-	-	9	S U	15	S C
OTHER ORGANISMS											
Elodea canadensis		24-h IC50[3]	-	24	-	-	-	1.43	S U	7	S A
		24-h IC90[3]	-	24	-	-	-	2.75	S U	7	S A
		28-d EC50[4]	-	24	-	-	-	2.0	S* U	7	S C
Lemna minor		14-d EC50[4]	-	-	-	-	-	0.008	S* U	7	S C
		10-d EC50[8]	-	-	-	-	-	0.04	R M	13	S C
		10-d EC50[9]	-	-	-	-	-	0.03	R M	14	S C
		10-d EC50[10]	-	-	-	-	-	0.04	R M	14	S C
		10-d EC50[8]	-	-	-	-	-	0.05	R M	14	S C

TABLE 2: AQUATIC TOXICITY DATA TABLE FOR THALLIUM .....Continued

SPECIES	LIFE STAGE	RESPONSE	TEST CONDITIONS pH	TEMP (°C)	DO (mg/L)	ALK. (mg/L)	HARD. (mg/L)	EFFECT CONC. (mg/L)	DATA CODES KEY(1)	DATA REF KEY(3)	DATA QUALITY KEY(2)
Selenastrum capricornutum		96-h EC50[5]	-	-	-	-	-	0.11	S -	4	S C
		96-h EC50[6]	-	-	-	-	-	0.1	S -	4	S C
Chlamydomonas reinhardtii		I40[4]	-	-	-	-	-	40.8	S U	9	S C
Anacystis nidulans		96-h TC[11]	-	-	-	-	-	3	S U	15	S C
Chlorella vulgaris		96-h TC[11]	-	-	-	-	-	3	S U	15	S C

KEY (1):

F = flowthrough
R = renewed static
S = static
M = measured toxicant concentrations
U = unmeasured toxicant concentrations
NP= not presented

KEY (2):

P = primary
S = secondary
A = acute toxicity
C = chronic toxicity

KEY (3) REF. NO.

1 Zitko *et al.* (1975)
2 Nehring (1962)
3 LeBlanc and Dean (1984)
4 USEPA (1980)
5 Dilling and Healey (1926)
6 Birge (1978)
7 Brown and Rattigan (1979)
8 Dawson *et al.* (1977)
9 Overnell (1975)
10 Buccafusco *et al.* (1981)
11 LeBlanc (1980)
12 Kimball (MS) also cited in USEPA (1980)
13 Smith and Kwan 1989
14 Kwan and Smith 1988
15 DiGaudio 1975

Footnotes

[1] incipient lethal level
[2] endpoint was survival
[3] endpoint was O_2 evolution
[4] endpoint was damage in whole plants - concentration inhibiting respiration by 40%
[5] endpoint was inhibition of chlorophyll *a*
[6] endpoint was decrease in cell number
[8] endpoint was decrease in frond number
[9] endpoint was decrease in frond area
[10] endpoint was decrease in frond weight
[11] threshold concentration
* not clearly documented in the paper

Table 3: UNCERTAINTY FACTOR WORKSHEET

CHEMICAL:	CAS No	CONCENTRATION UNITS
Thallium	7440-28-0	mg/L

Test Conditions		Species (life stage)	Toxicity End Point	Effect conc.	Data Codes	Data Type	Calibration Factor	No. and Reference
ACUTE	VERTEBRATE	Fathead minnow 8 wk old	8d-LC50	1.45	FM	1°	0.8	Kimball MS
		Bluegill sunfish 0.32-1.2g	96h-LC50	120	SU	2°	0.9	Buccafusco et al. 1981
		Atlantic salmon fry	96h-LC50	1.4 (est.)	FM	2°	0.9	Zitko et al. 1975
	INVERT.	*Daphnia magna*	48h-LC50	0.91	SM	1°	0.8	Kimball MS
		Gammarus sp.	48h-LC100	4	SU	2°	0.9	Nehring 1962
CHRONIC	VERTEBRATE	Rainbow trout embryo-larval	28d-LC50	0.17	RM	1°	0.5	Birge 1978
		Fathead minnow day old	28d (p.h.) growth	0.081	FM	1°	0.5	Kimball MS
		Goldfish embryo-larval	7d-LC50	7	RM	1°	0.5	Birge 1978
	INVERT.	*Daphnia magna*	96h-LC50	0.68	SM	1°	0.5	Kimball MS
		Paramecium bursaria	96h-TC	9	SU	2°	0.9	DiGaudio 1975
	PLANT	*Lemna minor*	28d-EC50 (damage)	0.008	SU.	2°	0.9	Brown & Rattigan 1979

CALCULATION OF FINAL UNCERTAINTY FACTOR:

The Baseline Uncertainty Factor = 1000 since whole body bioconcentration factors in fish were < 1000

Baseline Uncertainty Factor X Calibration Factors (maximum number = 11)

1000 x .8 x .9 x .9 x .8 x .9 x .5 x .5 x .5 x .5 x .9 x .9

= 23.6 FINAL UNCERTAINTY FACTOR (NOT TO BE LESS THAN A VALUE OF 13)

CRITICAL VALUE ÷ FINAL UNCERTAINTY FACTOR = IPWQO

= 0.008 ÷ 24 = 0.0003 mg/L

Assign 2 DATA CODES, one from each of the following rows

S = static R = static/renewal F = flowthrough
U = unmeasured nominal conc M = measured conc
p.h. = post hatch

DATA TYPE

1° = Primary 2° = Secondary 3° = Simulated Data
? = Unknown (Default Data Quality = 2°)

tl-tbl3.drw

Figure 1: Thallium aquatic toxicity - cumulative percent versus concentration for laboratory studies.

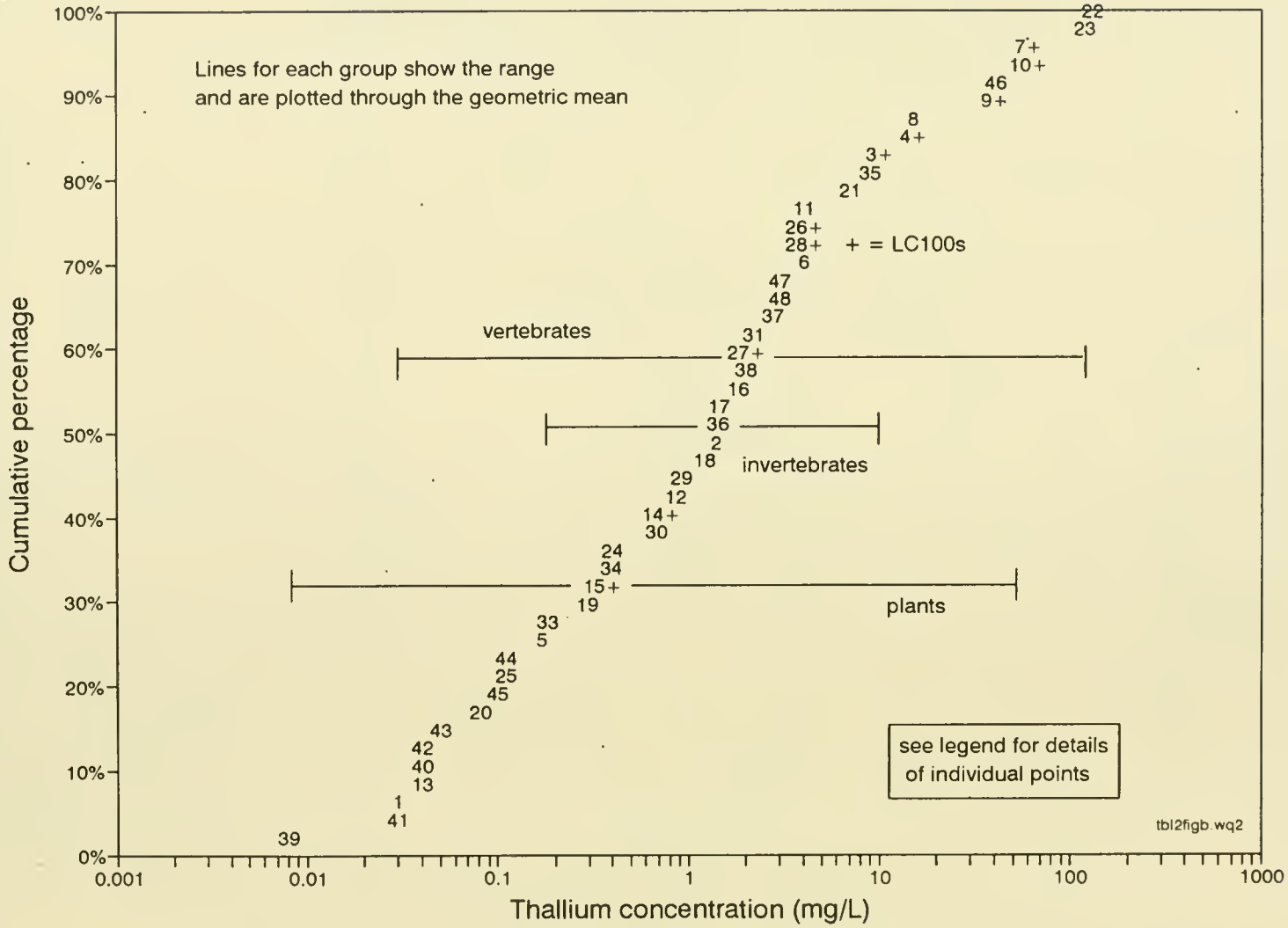
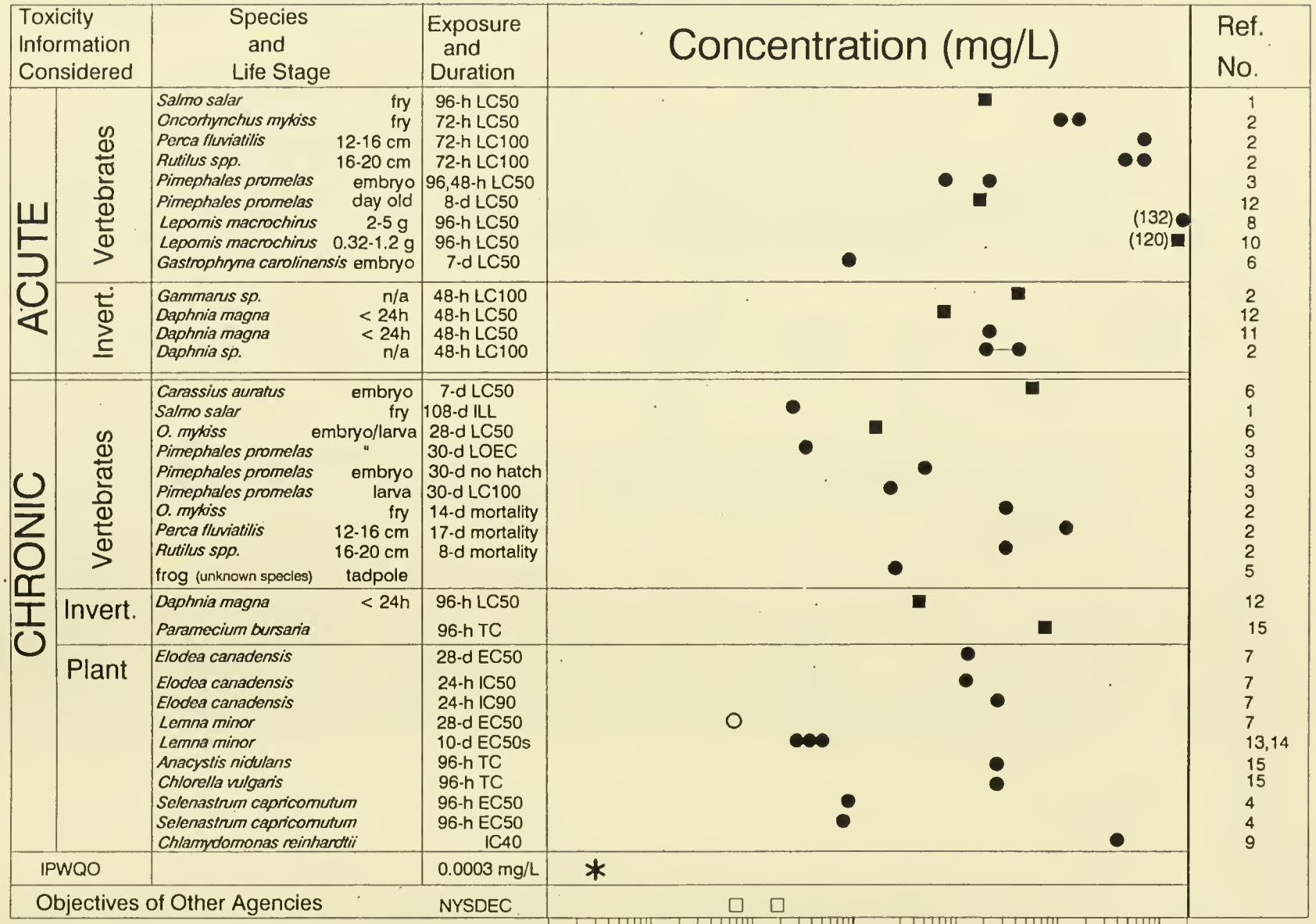


Figure Legend

Figure 1: Thallium aquatic toxicity - cumulative percent versus concentration for laboratory studies.

Data point		Species	Endpoint	Effect Concentration (mg/L)	Reference
1	fish	Atlantic salmon	108-d ILL	0.03	Zitko et al. 1975
2		Atlantic salmon	96-h LC50	approx. 1.4	Zitko et al. 1975
3		Rainbow trout	72-h LC100	10-15	Nehring 1962
4		Rainbow trout	72-h LC100	10-15	Nehring 1962
5		Rainbow trout	28-d LC50	0.17	Birge 1978
6		Rainbow trout	14-d mortality	4	Nehring 1962
7		Perch	72-h LC100	60	Nehring 1962
8		Perch	17-d mortality	15	Nehring 1962
9		Roach	72-h LC100	40-60	Nehring 1962
10		Roach	72-h LC100	40-60	Nehring 1962
11		Roach	8-d mortality	4	Nehring 1962
12		Fathead minnow	96-h LC50	0.86	LeBlanc and Dean 1984
13		Fathead minnow	30-d LOEC	0.04	LeBlanc and Dean 1984
14		Fathead minnow	no hatch	0.72	LeBlanc and Dean 1984
15		Fathead minnow	30-d LC100	0.35	LeBlanc and Dean 1984
16		Fathead minnow	4-d LC50	1.8	Kimball (undated)
17		Fathead minnow	8-d LC50	1.45	Kimball (undated)
18		Fathead minnow	68% abnormal at	1.2	Kimball (undated)
19		Fathead minnow	45% survival at	0.292	Kimball (undated)
20		Fathead minnow	28-d posthatch gr	0.081	Kimball (undated)
21		Goldfish	7-d LC50	7	Birge 1978
22		Bluegill sunfish	96-h LC50	132	Dawson et al. 1977
23		Bluegill sunfish	96-h LC50	120	Buccafusco et al. 1991
24	amphibian	Frog (sp. unknown)	-	0.4	Dilling and Healey 1926
25		Narrow mouth toad	7-d LC50	0.11	Birge 1978
26	invertebrate	*Gammarus sp*	48-h LC100	4	Nehring 1962
27		*Daphnia sp*	48-h LC100	2	Nehring 1962
28		*Daphnia sp*	48-h LC100	4	Nehring 1962
29		*Daphnia magna*	48-h LC50	0.91	Kimball (undated)
30		*Daphnia magna*	96-h LC50	0.68	Kimball (undated)
31		*Daphnia magna*	48-h LC50	2.2	LeBlanc 1980
33		*Daphnia magna*	lifecycle reprodu	0.181	Kimball (undated)
34		*Daphnia magna*	28-d LC50	0.393	Kimball (undated)
35	protozoa	*Paramecium bursaria*	96-h TC	9	DiGaudio 1975
36	plants/algae	*Elodea canadensis*	24-h IC50	1.43	Brown and Rattigan 1979
37		*Elodea canadensis*	24-h IC90	2.75	Brown and Rattigan 1979
38		*Elodea canadensis*	28-d EC50	2.0	Brown and Rattigan 1979
39		duckweed	14-d EC50	0.008	Brown and Rattigan 1979
40		duckweed	10-d EC50	0.04	Smith and Kwan 1989
41		duckweed	10-d EC50	0.03	Kwan and Smith 1988
42		duckweed	10-d EC50	0.04	Kwan and Smith 1988
43		duckweed	10-d EC50	0.05	Kwan and Smith 1988
44		*Selenastrum capricornutum*	96-h EC50	0.11	USEPA 1980
45		*Selenastrum capricornutum*	96-h EC50	0.1	USEPA 1980
46		*Chlamydomonas reinhardtii*	140	40.8	Overnell 1975
47		*Anacystis nidulans*	96-h TC	3	DiGaudio 1975
48		*Chlorella vulgaris*	96-h TC	3	DiGaudio 1975

FIG. 2: DERIVATION GRAPH - THALLIUM


Toxicity Information Considered
Species and Life Stage
Exposure and Duration
Concentration (mg/L)
Ref. No.
ACUTE
Vertebrates
Salmo salar fry 96-h LC50 1
Oncorhynchus mykiss fry 72-h LC50 2
Perca fluviatilis 12-16 cm 72-h LC100 2
Rutilus spp. 16-20 cm 72-h LC100 2
Pimephales promelas embryo 96,48-h LC50 3
Pimephales promelas day old 8-d LC50 12
Lepomis macrochirus 2-5 g 96-h LC50 (132) 8
Lepomis macrochirus 0.32-1.2 g 96-h LC50 (120) 10
Gastrophryne carolinensis embryo 7-d LC50 6
Invert.
Gammarus sp. n/a 48-h LC100 2
Daphnia magna < 24h 48-h LC50 12
Daphnia magna < 24h 48-h LC50 11
Daphnia sp. n/a 48-h LC100 2
CHRONIC
Vertebrates
Carassius auratus embryo 7-d LC50 6
Salmo salar fry 108-d ILL 1
O. mykiss embryo/larva 28-d LC50 6
Pimephales promelas " 30-d LOEC 3
Pimephales promelas embryo 30-d no hatch 3
Pimephales promelas larva 30-d LC100 3
O. mykiss fry 14-d mortality 2
Perca fluviatilis 12-16 cm 17-d mortality 2
Rutilus spp. 16-20 cm 8-d mortality 2
frog (unknown species) tadpole 5
Invert.
Daphnia magna < 24h 96-h LC50 12
Paramecium bursaria 96-h TC 15
Plant
Elodea canadensis 28-d EC50 7
Elodea canadensis 24-h IC50 7
Elodea canadensis 24-h IC90 7
Lemna minor 28-d EC50 7
Lemna minor 10-d EC50s 13,14
Anacystis nidulans 96-h TC 15
Chlorella vulgaris 96-h TC 15
Selenastrum capricornutum 96-h EC50 4
Selenastrum capricornutum 96-h EC50 4
Chlamydomonas reinhardtii IC40 9
IPWQO 0.0003 mg/L
Objectives of Other Agencies NYSDEC
0.0001 0.001 0.01 0.1 1 10 100
✳- IPWQO
○- Critical Velue
●- Single species endpoint
■- Uncertainty factor modifying endpoint
△- Odour Protection Values
□- Objectives of Other Agencies

tl-fig2a.drw

Table 4. Summary Details From Critical Toxicity Paper

Chemical	thallium sulphate
Reference	Brown and Rattigan 1979
Species common name	duckweed
Scientific name	*Lemna minor*
Organism age/size	actively growing
Exposure duration	14 days
PWQO data classification	secondary
PWQO duration classification	chronic
Endpoint	50% plant damage
Effect concentration	0.008 mg/L
Static/renewal/flow-through	static
Number concentration levels/controls	unknown
Number test organisms per concentration	10 replicates
Chemical purity	not stated
Test container	plastic cup
Volume of test solution	300 mL
Measures taken to prevent volatilization	non-volatile
Water type	distilled water plus added major ions in 5 mM HEPES buffer
Test solution characteristics - pH	6.7-7.6
- temperature	probably 24°C
- dissolved oxygen	varied with photosynthetic activity
- hardness (mg/L $CaCO_3$)	100 mg/L (calculated)
- alkalinity (mg/L $CaCO_3$)	not stated